High Resolution FTIR Measurements of Voigt Half-Widths of CO_2 Broadened by H_2O at 4.3 μm

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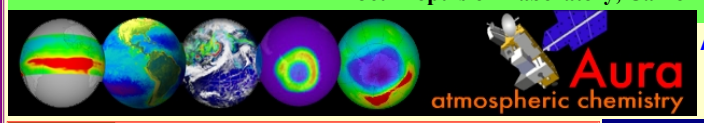

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Abstract To support remote sensing of CO_2 in the tropics, H_2O-broadened half-widths were obtained for 182 lines of $^{12}CO_2$ (v_3, $v_2+v_3-v_2$) and $^{13}CO_2(v_3)$ bands between 2250 – 2390 cm^{-1}.

☑ For this, six spectra were recorded at 0.00389 cm^{-1} resolution (unapodized) using a Bruker IFS-125HR at JPL.

☑ widths of CO_2 broadened by O_2, N_2 or CO_2 decrease with rotational quantum number J, but H_2O-broadened half-widths follow behavior predicted from theory: ~ 0.12 cm^{-1}/atm at low J, increasing to ~ 0.145 cm^{-1}/atm near J = 55 and decreasing J > 55.

☑ Therefore, additional H_2O-broadening should be taken into account in the modeling of tropospheric CO_2.

☑Since little vibrational dependence is seen for the three bands, these in line broadening at 4.3 μm can be applied to all CO_2 transitions.

▶Why we study H_2O-broadened CO_2 half widths?

♣ The Orbiting Carbon Observatory (OCO) mission and the Greenhouse Gases Observing Satellite (GOSAT) mission will measure the regional differential distribution of CO_2 concentration with sub-percent precision so that higher accuracy is needed for spectroscopic line parameters. The requirement for pressure-broadened line widths is better than 0.6% [1].

♣ For such accuracy, CO_2 line broadening by ambient H_2O must be included because

(a) Atmospheric CO_2 is dominantly present in the lower boundary as is the same for H_2O vapor, so CO_2 line broadening by H_2O is unavoidable.

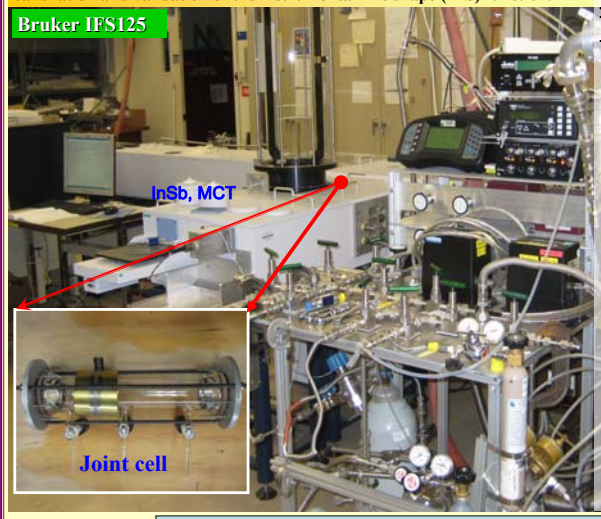
(b) H_2O vapor can be up to 5% in the warmest regions [2] and ~ 1 − 3% near the surface in the middle latitudes [3].

(c) H_2O-broadened CO_2 half-widths could be twice air broadening according to a theory [4].

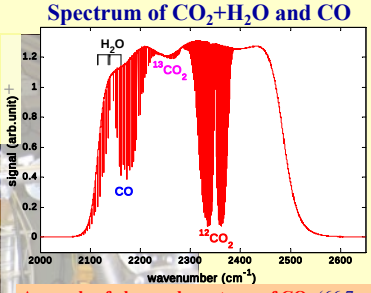
♣ Direct measurement of H_2O-broadened CO_2 half-width is limited, and we have measured the H_2O-broadened half widths of $^{12}CO_2$ (v_3 and $v_2+v_3-v_2$) and $^{13}CO_2(v_3)$ bands for the first time using a Fourier transform spectrometer.

Experimental set-up and conditions

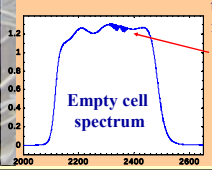
Spectra were obtained using the Fourier transform spectrometer and a custom-made joint cell of Pyrex consisting of two sub-cells in tandem sharing one of the CaF_2 windows. The shorter cell was 6.14 cm long and held the CO_2 H_2O mixtures; the other, 15.26 cm long, contained CO for frequency calibration and validation of the instrumental line shape (ILS) function.



Spectrum of CO_2+H_2O and CO



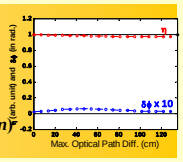
A sample of observed spectrum of CO_2 (66.7 mtorr) broadened by H_2O (20.9 torr) at 299.7 K. Note that CO and CO_2 in a different sub-cell were recorded at the same time, and that the CO_2 hot band is also visible near 2340 cm^{-1}. A few weak lines (*e.g.* 2136.14, 2161.73 cm^{-1}) from H_2O (v_2) band appear , but these were not strong enough to determine the H_2O vapor pressure. CO_2 (v_3) is a very strong band so that the residual CO_2 in the IFS resulted in absorption features whose optical depths are < ~3%, which were retrieved simultaneously in the spectrum fitting.



Data analysis

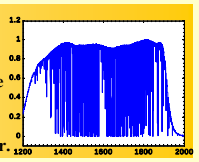
Instrumental Line Shape (ILS) Function

- Derived from CO (1-0) lines using LINEFIT (v.11, [5])
- The modulation efficiency, η, ~ 0.98 and residual phase errors, δφ, ~ 0.2°, resulting in insignificant instrumental line broadening and line shape distortion
- Therefore, in actual retrieval, a nominal ILS (*sinc function*) with FOVcorrection was used.



Determination of H_2O partial pressure in the mixtures

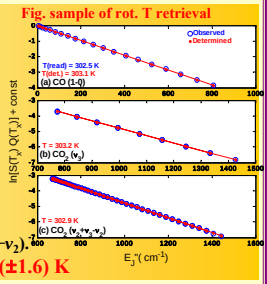
- Recorded v_2 water transitions near 6 μm from the same CO_2+H_2O mixture using the MCT detector.
- The intensities of 13 unblended, temperature-insensitive v_2 transitions were retrieved.
- Compared to Coudert et al.'s values [6]
- Derived H_2O partial pressures are from 20.1 to 26.5 torr.



Validation of the cell temperatures

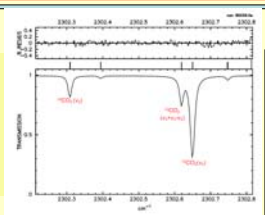
- Rotational temperatures were derived by $\ln\{(S_X Q_X)/(S_R Q_R)\}/C_2 = E''/T_R - E''/T_X$,
  E" is lower state energy (cm^{-1}),
  S_X measured line intensity,
  S_R the reference intensity (cm^{-1}/ molecule·cm^{-2}) at T_R = 296K taken from the HITRAN 2004
  T_X is the expr. temperature to be determined.
  Q the rovibrational partition functions
  C_2 = 1.4388 (cm·K).
- Three different bands were used: (a) CO (1−0), (b) $^{12}CO_2$ (v_3) and (c) CO_2 ($v_2+v_3-v_2$).
- The mean temperature of the six runs is 301.5 (±1.6) K

Fig. sample of rot. T retrieval

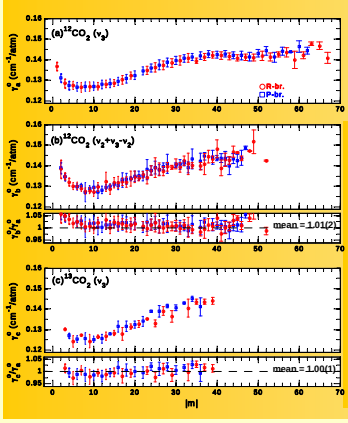


Retrievals and Results

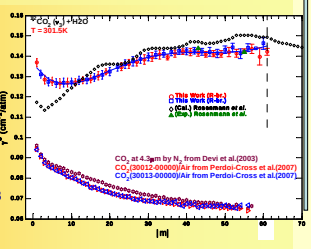
Non-linear least square retrievals Line center position, line intensity, and broadening coefficients were retrieved by adopting Voigt line shape function with no line mixing considered. The retrievals were conducted spectrum by spectrum, and fitting residuals less than 0.2% was achieved as shown in a sample plot.
Note that virtual lines were retrieved simultaneously to include the extra absorption features originating from the residual CO_2 in the IFS.



Measured half-width coefficients at 301.5 (±1.6) K for (a) γ_a for v_3 and (b) γ_b for $v_2+v_3-v_2$ of $^{12}CO_2$, and (c) γ_c for v_3 of $^{13}CO_2$. The ratios of the half-widths, γ_b/γ_a and γ_c/γ_a are seen to be close to unity and their mean values are 1.01 (±0.02) and 1.00(±0.01), respectively. These ratios suggest that there is only a small dependence of the half-widths on the vibrational lower states in the 2250 − 2300 cm^{-1} region, similar to what was observed in other bands of CO_2 and its isotopologues and in other molecules.

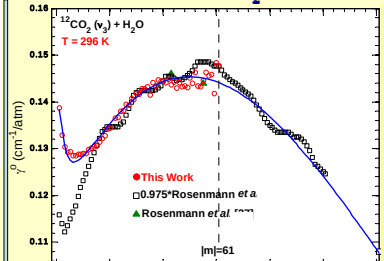


Comparison of measured H_2O pressure-broadened CO_2 half-widths with the calculations by Rosenmann et al. [4] and the two diode laser measurements for R42 and R54 by Rosenmann et al. [7]. The solid line represents the polynomial-fit half-widths based on the present measurements for |m| ≤ 61. All the widths are compared at 301.5 K.



Comparison with N_2- and Air-broadened half widths at 296 K.
H_2O broadening reaches almost twice of the values by N_2 and air.

Recommended H_2O-broadened half-widths at 296 K



By combining measurements from this work (|m| ≤ 61) and Rosenmann et al.[4]'s calculations (|m|>61) with a slight adjustment, a recommended set was constructed at 296 K. The diode laser measurements of R42 and R54 at 296 K from Ref.[7] are in excellent agreement. Finally we present calculated half-widths fit to $F(|m|)=a/m^2+b/|m|+d|m|+em^2+f|m|^3+c$, a = −0.03563, b = 0.06318, d = 0.001498 e = −1.848×10^{-5}, f = 4.924×10−8, c = 0.1093 which is valid up to |m| ≤ 121.

Conclusion

♫ Measured H_2O-broadened half-widths of $^{12}CO_2$ (v_3, $v_2+v_3-v_2$) and $^{13}CO_2(v_3)$, which were observed to reach almost twice the values by air in the intermediate m.

♫ Constructed recommended set of the half-widths at 296 K.

♫ These widths can be used for other bands of $^{12}CO_2$ and its isotopologues.

♫ These results will reduce systematic errors in measurements of tropospheric CO_2.

♫ Water broadening of other tropospheric molecules, such as CH_4, N_2O, and O_2, maybe needed as well.

Selected References:

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[3] T. Wagner, J. Heland, M. Zoger, and U. Platt, Atmos. Chem. Phys. 3, 651 (2003).
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